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Use of Hydrochloric Acid for Determining Solid-Phase Arsenic Partitioning in Sulfidic Sediments

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We examined the use of room-temperature hydrochloric acid (1−6 M) and salt solutions of magnesium chloride, sodium carbonate, and sodium sulfide for the removal of arsenic from synthetic iron monosulfides and contaminated sediments containing acid-volatile sulfides (AVS). Results indicate that acid-soluble arsenic reacts with H_2S released from AVS phases and precipitates at low pH as disordered orpiment or alacranite. Arsenic sulfide precipitation is consistent with geochemical modeling in that conditions during acid extraction are predicted to be oversaturated with respect to orpiment, realgar, or both. Binding of arsenic with sulfide at low pH is sufficiently strong that 6 M HCl will not keep spiked arsenic in the dissolved fraction. Over a wide range of AVS concentrations and molar [As]/[AVS] ratios, acid extraction of arsenic from sulfide-bearing sediments will give biased results that overestimate the stability or underestimate the bioavailability of sediment-bound arsenic. Alkaline solutions of sodium sulfide and sodium carbonate are efficient in removing arsenic from arsenic sulfides and mixed iron−arsenic sulfides because of the high solubility of arsenic at alkaline pH, the formation of stable arsenic complexes with sulfide or carbonate, or both.

Introduction

Determining the solid-phase partitioning of metal and metalloid elements in sediments and soils is an important component of contaminant transport and fate investigations at hazardous waste sites. Quantitative assessments of metal−mineral associations allow for predictions of contaminant stability, mobility, and bioavailability that are necessary for selecting the most efficient and cost-effective site remedies. Arsenic partitioning to sediment matrixes is especially dependent on the oxidation−reduction (redox) state, which governs arsenic distribution between As(V) and As(III) in aquatic environments. In addition, the redox state influences the geochemical and microbiological cycling of iron and sulfur, element cycles to which arsenic transport and fate are inexorably tied (*1*, *2*).

In sulfate-reducing environments, As(III) is potentially associated with an assortment of poorly crystalline to crystalline iron oxides, iron sulfides, or discrete arsenic sulfides, such as orpiment (As_2S_3) (*3*−*9*). Based upon the results of chemical extractions and microanalytical techniques, trace metals (Co, Ni, Cu, Zn, Mo, Cd, Sb, Hg, Mn) are frequently found associated with pyrite (FeS_2) in organic-rich sediments (*10*). In particular, As, Hg, and Mo are generally enriched in pyrite relative to bulk sediments (*10*, *11*). The formation of pyrite in freshwater and marine sediments proceeds through metastable iron monosulfide precursors, i.e., disordered mackinawite, mackinawite, and greigite (*12*−*15*). Consequently, it may be reasonable that arsenian pyrite forms via the transformation of an arsenic-bearing iron monosulfide precursor.

Chemical extraction procedures are perhaps the most frequently used and most generally applicable tools to assess metal associations in anoxic sediments (*16*, *17*). In many proposed extraction procedures, hydrochloric acid is used to target metals associated with iron monosulfides and coprecipitated iron−metal monosulfides. This approach is based upon the following general solubility-controlling reaction of metal monosulfide minerals:

$$\mathrm{MeS(s)} + 2\mathrm{H}^+ = \mathrm{Me}^{2+} + \mathrm{H_2S(aq)}$$

where Me represents a divalent metal (e.g., Cd, Cu, Fe, Pb, and Zn). At low pH, metal monosulfides dissolve and yield metal cations and hydrogen sulfide gas; hence, they are referred to as acid-volatile sulfides (AVS). In a related application, toxicity to benthic animals in anoxic sediments is estimated by determining the molar ratio of AVS to simultaneously extracted metals (SEM) released from sediments by reaction with hydrochloric acid (*18*). If [AVS]/[SEM] > 1, then it is assumed that metal concentrations in porewaters should be low because of the insolubility of metal sulfides at near-neutral pH typical of sediment porewater. Conversely, a molar ratio of less than 1 suggests that sediments are depleted in the sulfide necessary to sequester metals, indicating a potential risk to sediment-dwelling organisms. However, for certain metals that form very insoluble sulfide precipitates (e.g., Hg and Cu), hydrochloric acid may not be an effective extractant and it has been suggested that in many cases the AVS/SEM model should be cautiously applied (*19*−*22*).

The use of HCl extractions and the application of the AVS/SEM model have been extended to evaluations of arsenic partitioning and toxicity in sediments (e.g., refs *23*−*26*). In this context, it needs to be pointed out that arsenic chemical behavior in sulfidic environments contrasts with the behavior of d-transition metals as indicated by inspection of possible solubility-controlling reactions for orpiment:

$$\mathrm{As_2S_3(s)} + 6\mathrm{H_2O} = 2\mathrm{H_3AsO_3(aq)} + 3\mathrm{H_2S(aq)}$$

and

$$\mathrm{As_2S_3(s)} + \mathrm{H_2S(aq)} = 2\mathrm{AsS_2}^- + 2\mathrm{H}^+$$

where the dominant As(III) soluble species are arsenite and thioarsenite, respectively. Note that, in these reactions, orpiment solubility is expected to be independent of pH or decrease with decreasing pH. These trends contrast with MeS solubility behavior as noted above. It may be expected that, upon acidification, systems containing arsenic and sulfide will precipitate as arsenic sulfide, and in fact, low-pH synthesis of orpiment has been utilized in previous solubility studies in the As−S−H_2O system (*27*, *28*). It follows that under some conditions precipitation at low pH may pose problems for using acid extractions to evaluate arsenic speciation in sulfidic sediments and to assess sediment toxicity with respect to arsenic. In addition, it is possible that the assimilative

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capacity of sediment invertebrates in AVS-bearing sediments may be low due to the decreased solubility of arsenic sulfide at gut pH (*29*). In this study, we examine the chemical extraction behavior of arsenic in sulfidic sediments using geochemical modeling and experimental approaches.

Experimental Section

Geochemical Modeling. To evaluate the potential for metal reprecipitation during extraction, we performed solubility calculations using MinteqA2 (*30*). The MinteqA2 thermodynamic database was updated to include commonly accepted solubility constants for disordered and crystalline metal sulfides and formation constants for both the fully protonated and deprotonated form of thioarsenite (see Supporting Information). Calculations were performed for a hypothetical extraction experiment consisting of a 0.4-g sediment sample with predefined concentrations of iron monosulfide and associated contaminant metals suspended in 40 mL of a 2 M NaCl solution with a pH range of 0.1−10. The Davies equation was employed for ion activity corrections. During modeling, precipitation was not allowed to occur. We documented the resultant saturation index (SI) for a suite of relevant metal sulfides. For SI > 0, it is assumed that precipitation could take place instantaneously as a result of H_2S release during iron monosulfide dissolution. The modeling exercises assume that all H_2S released from dissolving AVS materials is retained in solution (closed system), as might the case in a batch or sequential extraction procedure. In practice, H_2S is sometimes purged from the acid extractant solution using an inert gas (open system) and in this case the dynamic processes governing H_2S concentrations are incompletely accounted for in the equilibrium modeling. The model results are therefore taken to reflect the maximum potential for sulfide mineral precipitation during an acid extraction.

FeS Synthesis. Iron monosulfides were prepared by mixing into sealed airtight glass bottles (43 mL) equivalent volumes of 0.1 M ferrous ammonium sulfate and sodium bisulfide solutions. All solutions were prepared using deoxygenated and distilled water (Milli-Q). Removal of dissolved oxygen to concentrations <0.2 mg L^{-1} was verified by using rhodazine D colorimetric test kits (Chemetrics, K-7501). Sodium bisulfide solutions were prepared by purging 0.1 M NaOH with a 1 vol % hydrogen sulfide gas mixture (balance nitrogen) (*14*). Sodium arsenite in aqueous solution was added to the suspension to bring initial arsenic concentrations to between 0.03 and 3 mM. The resulting inky-black suspension was aged at room temperature for 24 h in the dark. In all syntheses, final pH of the suspension was between 6 and 8.5 and great care was taken to avoid exposure of the sulfide precipitates to the atmosphere. Solutions were undersaturated with respect to disordered orpiment, and the suspension density was ~4 mg mL^{-1}. The precipitated metal sulfides were not freeze-dried. Freeze-drying significantly affects the reactivity of iron monosulfides (*15*) and causes oxidative loss of concentrations of acid-extractable sulfide (*21*). Instead, aliquots of the suspensions were withdrawn and immediately used in extraction studies or iron monosulfide suspensions were filtered in an anaerobic glovebox, dried under a stream of nitrogen gas, and the solids used in extraction experiments.

Sediment Samples. Sediment samples were collected from Halls Brook Holding Area (HBHA) pond located adjacent to the Industri-Plex Superfund site situated in the headwaters of the Aberjona watershed (Woburn, MA). The upper, organic carbon- and AVS-rich (1.68 ± 0.08 wt %) sediments of the HBHA pond contain elevated concentrations of arsenic and other metals due to groundwater transport and deposition of contaminants. Surface sediments were sampled directly into plastic bags and frozen immediately after collection until analysis. In the laboratory, the frozen sediments were thawed in an anaerobic chamber and sediment porewater was decanted. The residual sediment was dried under a N_2-H_2 atmosphere at room temperature and finally ground gently with an agate mortar and pestle.

Extraction Procedures. Extraction experiments were conducted at room temperature in 20-mL plastic vials or in a 500-mL glass reaction kettle. Quantities of FeS precipitates (~10 mg), sediments (~100 mg), or sediment plus quartz sand mixtures (~100 mg) were added to the plastic vials in a glovebox and mixed with 10 mL of HCl (1, 3, or 6 M), 6 M HCl with 15% by weight $SnCl_2$, 1 M $MgCl_2$, 0.1 M Na_2CO_3, or 0.1 M Na_2S. The larger volume kettle was needed in experiments where the mass of precipitated FeS and volume of HCl was increased proportionately in order to collect enough residual material for analysis. Some sediment samples were spiked prior to acid extraction with additions of fresh arsenite solutions prepared from $NaAsO_2$. Chemical extractions were conducted on a mechanical shaker under a nitrogen atmosphere. Reaction time varied from 1 to 24 h. After extraction, residual solids were filtered under nitrogen and dried. Supernatant solutions were filtered through 0.2-μm syringe filters (cellulose acetate) and acidified with ultrapure nitric acid prior to analysis. Prior to arsenic determinations after Na_2S extractions, sulfide was oxidized to prevent precipitation of elemental sulfur and arsenic sulfides. Hydrogen peroxide (30%) was added to oxidize sulfide to sulfate and then acid was added to bring the pH below 2.

Analyses. Concentrations of total arsenic and other metals were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 3300 DV) or by graphite furnace atomic absorption spectroscopy (GFAAS, Perkin-Elmer 5100PC). AVS and chromium reducible sulfur (CRS) were determined by sequential acid distillation of sediment samples using room-temperature 3 M HCl (AVS) followed by boiling 1 M $CrCl_2$ plus 0.5 M HCl (CRS) (*31*, *32*). The amount of hydrogen sulfide released was quantitatively determined using a sulfur coulometer (UIC, Inc.). The synthetic sulfides were characterized by powder X-ray diffraction (XRD, Rigaku Miniflex); mackinawite precipitates were mixed with glycerol to prevent oxidation during analysis and mounted in an anaerobic glovebox on a zero-background quartz plate. Concentrations of selected metals in sediment samples were determined by X-ray fluorescence spectrometry (XRF, Jordan Valley EX-310). The accuracy of the XRF measurements was verified by using standard USGS reference materials.

Results and Discussion

Modeling Results. The results of thermodynamic modeling for a hypothetical sediment containing 0.1 wt % FeS with 100 μg g^{-1} As, Cu, and Zn are shown in Figure 1. These concentrations are reasonable for contaminated sediments formed under iron- and sulfate-reducing conditions (*33*). The predicted saturation index of relevant metal sulfides is shown in Figure 1A. For pH <3, both FeS and ZnS are undersaturated, whereas As_2S_3 and CuS are oversaturated. As pH is increased, FeS and ZnS eventually become oversaturated in a closed system (pH 8.75 and 3.81, respectively). In contrast, As_2S_3 becomes undersaturated at pH 4.35, while CuS remains oversaturated over the entire pH range. The predominant aqueous arsenic species predicted over the entire pH range is H_3AsO_3 (Figure 1B). These observations are consistent with results of AVS/SEM extractions for FeS, ZnS, and CuS. Both FeS and ZnS are dissolved under the conditions commonly employed for AVS extraction (*20*−*22*), whereas CuS is not recovered in HCl extractions (*20*). At constant concentration of arsenic, the potential for precipitation decreases as concentrations of extractable sulfide fall

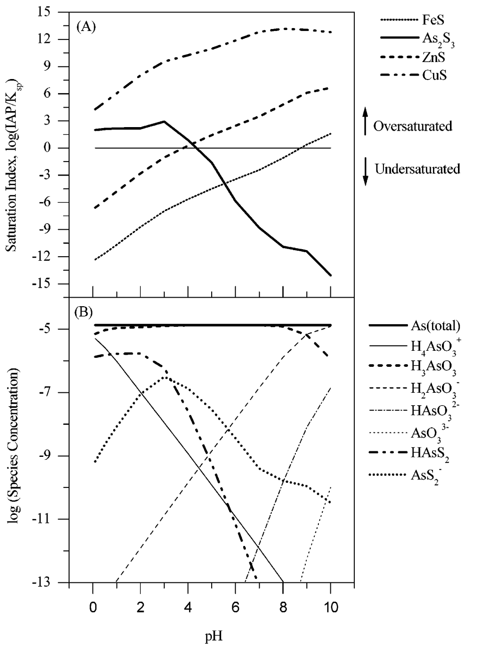

FIGURE 1. Results of thermodynamic modeling for a system containing 0.4 g of sediment with 0.1 wt % FeS and 100 μg g^{-1} of As (molar [As]/[AVS] = 0.12), Cu (molar [Cu]/[AVS] = 0.14), and Zn (molar [Zn]/[AVS] = 0.13). The FeS and associated metals were allowed to dissolve in a closed system containing 40 mL of 2 M NaCl over a range of pH. (A) Predicted saturation index as a function of pH for the mineral covellite (CuS) and the disordered forms of FeS, As$_2$S$_3$, and ZnS. (B) Predicted aqueous arsenic speciation as a function of pH.

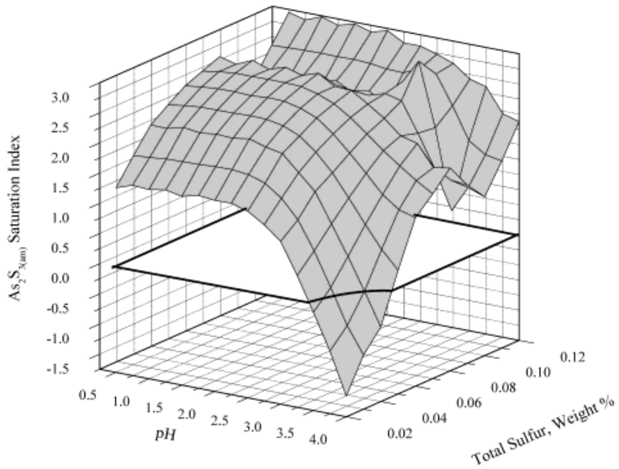

FIGURE 2. Contour of the As$_2$S$_{3(am)}$ saturation index (SI) as a function of pH and total sulfur. SI data were generated using MinteqA2 following database revision (see Supporting Information). The flat, outlined SI surface is coincident with SI = 0 for all pH and total sulfur contents. Intersection of this surface and the modeled experimental SI surface shows oversaturation of the extractant solution over a wide range of pH and total sulfur content (as extractible sulfides).

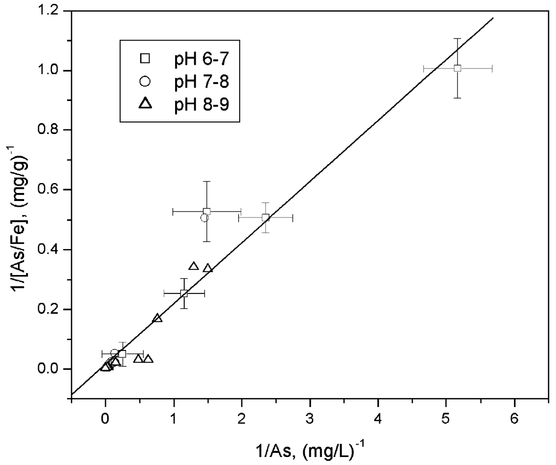

FIGURE 3. Arsenic adsorption to mackinawite (FeS) at variable pH. Data were fit to the linearized form of the Langmuir isotherm (*34*) by assuming monolayer coverage and a homogeneous distribution of adsorption sites.

below ~0.02 wt % (Figure 2), especially in materials where the molar concentration of arsenic approaches or exceeds that of AVS (see Supporting Information). Thermodynamic predictions clearly indicate that AVS extractions may be unsuitable for evaluating arsenic solid-phase speciation in sulfidic sediments, although it is acknowledged that the closed-system modeling approach may overpredict the extent of precipitation at low pH as described previously.

Arsenite Adsorption. X-ray diffraction analyses of synthetic iron monosulfide spiked with arsenite only showed broadened peaks corresponding to those present in crystalline mackinawite, results typical for pure iron sulfide precipitates aged at room temperature (*12−15*). Adsorption of arsenite on mackinawite is well described by a Langmuir-type adsorption isotherm (Figure 3). Adsorption behavior appears to be independent of pH from pH 6 to 8.5. Regression analyses indicate that surface saturation occurs at 0.15 mol of As/mol of FeS. Mackinawite with ~0.5 wt % sorbed arsenic (0.006 mol of As/mol of FeS) was used in the acid extraction experiments. Solutions in equilibrium with the FeS precipitates were highly undersaturated with respect to disordered orpiment ($-3.5 > \log(\mathrm{IAP}/K_{sp}) > -8.8$), evidence that sorption was the main uptake mechanism for arsenic and that orpiment was not present in the system prior to acid extraction. In addition to the high degree of undersaturation with respect to orpiment in the synthesis experiments, structural dissimilarity between orpiment and mackinawite points to adsorption as the principal arsenic uptake mechanism over the formation of a dilute solid solution.

Characterization of Extraction Residue. After extraction of mackinawite plus sorbed arsenic with 1−6 M HCl or 6 M HCl with 15% stannous chloride added, a residual solid was observed that varied in color from light reddish-tan to light greenish-yellow. Results of X-ray diffraction scans of the residual solids are shown in Figure 4. Chemical extraction of the arsenic-bearing iron sulfide with hydrochloric acid yields a poorly crystalline solid with broadened peaks at *d* spacings corresponding to 5.00, 2.89, and 1.67 Å (Figure 4, trace B). Similar reflections are prominent in a purchased powder of arsenic sulfide (As_2S_3, Aldrich) and would seem to be characteristic of an arsenic sulfide lacking a high degree of atomic ordering and with a chemical composition similar to that of orpiment (Figure 4, trace A). When stannous chloride was added to the hydrochloric acid, the resulting residual precipitate was identified as alacranite (As_4S_4) (Figure 4, trace C). Alacranite is a rare mineral species that has been identified in the mineral paragenesis of continental hydrothermal deposits enriched in mercury, antimony, and arsenic (*35, 36*). The addition of stannous chloride to hydrochloric acid solutions in AVS determinations is especially important for measurements in iron-rich sediments. Stannous ions rapidly reduce Fe(III) to Fe(II) and thereby prevent the oxidative loss of H_2S that can lead to underestimates of AVS values and overestimates (due to precipitation of S^0) of iron disulfide values that are determined by extraction with acidic chromous chloride (*37*). Apparently stannous chloride is also effective in reducing As(III) to As(II), which is the principal

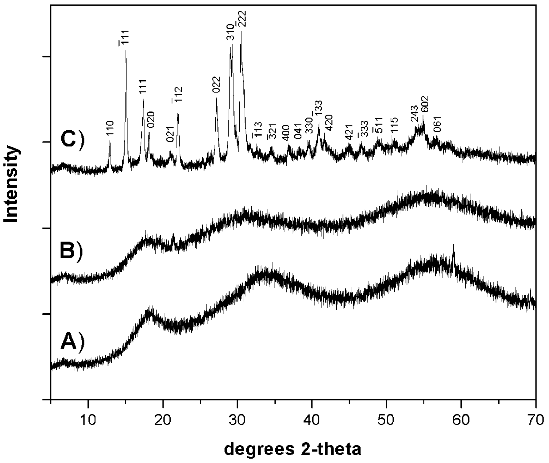

FIGURE 4. X-ray diffraction patterns for (A) As_2S_3 (99.9%, Aldrich), (B) residual solids after HCl extraction of mackinawite plus sorbed arsenic, and (C) residual solids after HCl + $SnCl_2$ extraction of mackinawite plus sorbed arsenic. Pattern C is indexed to JCPDS file 42-537 (alacranite).

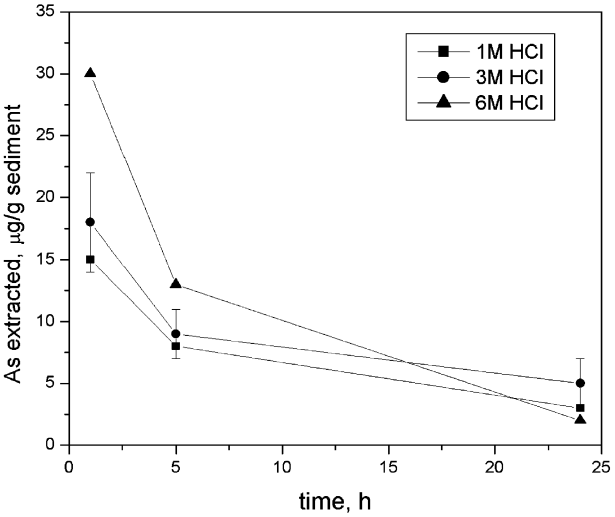

FIGURE 5. Arsenic extracted from HBHA pond sediment as a function of time and acid strength.

arsenic oxidation state in alacranite and realgar (AsS). Geochemical modeling results predict that realgar becomes more supersaturated compared to orpiment when E_h is fixed at values near the H_2/H_2O couple, a redox condition which approximately corresponds to that of a stannous chloride solution (see Supporting Information).

Experiments with HBHA Pond Sediments. Studies of iron and sulfur partitioning in sediments have utilized a wide range of hydrochloric acid concentrations in both single- and multiple-step extraction schemes. Berner (*12*) originally used boiling 12 M HCl (several minutes) to determine reactive iron concentrations in sediments. Leventhal and Taylor (*38*) found that 24-h extraction at room temperature with 1 M HCl leached amounts of iron comparable to that with boiling 12 M HCl. For AVS and SEM determinations, HCl concentrations from 0.5 to 6 M have been used in single-step experiments. Significant differences in the extractability of Hg and Cu have been noted depending on the choice of acid strength (*19, 20*). Extraction of AVS-rich sediments from the HBHA pond with 1−6 M HCl indicated that after 1 h of reaction increasing amounts of arsenic were released with increasing acid strength (Figure 5). Less than 5% of the total sediment arsenic was released to solution with 6 M HCl. With increasing extraction time, however, the yield of arsenic actually decreased, which is an entirely unexpected result and atypical for other metals commonly targeted with HCl extractions. Extraction results for other metals did not show the anomalous trend exhibited by arsenic. The time-dependent concentrations of Fe, Al, Mn, Cd, Pb, and Zn extracted with 1−6 M HCl solution were determined. For these elements, expected trends were observed; i.e., extraction yield increased with increasing time and acid strength (Figure 6). The observed differences in arsenic extracted with variable acid concentrations do not appear to be related to different sediment phases being leached. The time-dependent decrease in arsenic in the HCl extractant solutions is probably related to continued precipitation as AVS is released or due to aging of arsenic sulfide precipitates to more stable and less soluble forms of arsenic sulfide.

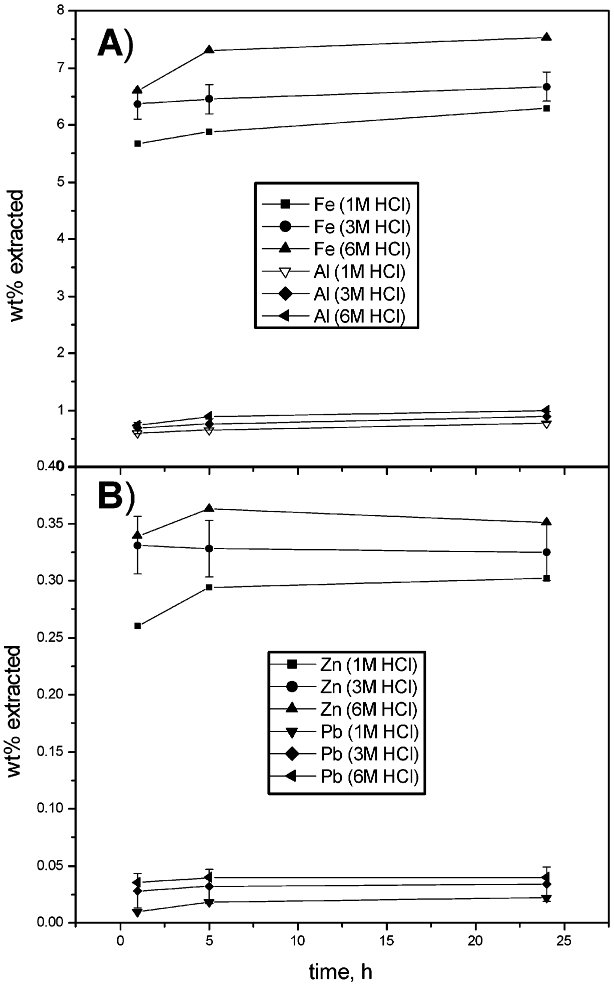

FIGURE 6. (A) Fe and Al, and (B) Zn and Pb extracted from HBHA pond sediment as a function of time and acid strength.

Recovery of pre-extraction spikes of arsenite to HBHA sediments is shown in Figure 7. Between 90 and 98% of the arsenite added was retained in the solid phase. Although the practice of spiking sediments and soils with quantities of trace metals prior to chemical extraction to determine extraction efficiency has yielded results often difficult to interpret (*39, 40*), the trend of decreasing arsenic yield with time (Figure 5) and the poor recovery from spiked experiments (Figure 7) strongly suggest that precipitation of arsenic during acid extraction was an important process at HCl concentrations of 1−6 M. Precipitation processes that occurred when synthetic iron monosulfides doped with arsenite reacted with acid were also likely occurring in the HBHA pond sediments during acid extraction.

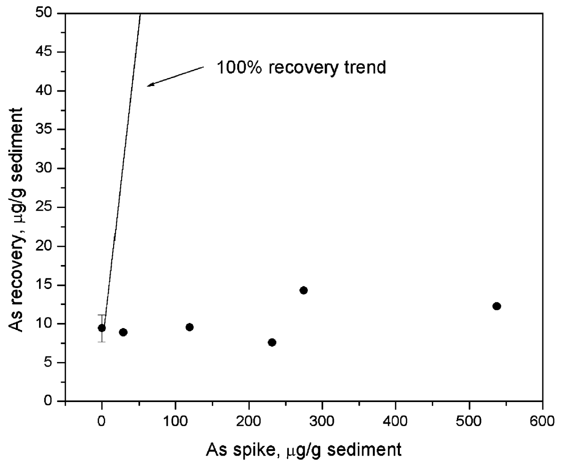

FIGURE 7. Recovery of pre-extraction arsenite spike from HBHA pond sediment after extraction with 3 M HCl for 5 h. The 100% recovery line indicates the trend expected if all spiked arsenite was recovered during acid extraction.

To explore the effects of decreasing AVS content and open- versus closed-system experiments on arsenic extraction results using hydrochloric acid, experiments were conducted on mixtures prepared by progressively adding HBHA pond sediment to quantities of fine-grained quartz sand (Fisher silica sand). Results of these sediment dilution experiments are plotted in Figure 8, where percent of arsenic, lead, and copper extracted is the calculated recovery of the acid extraction based upon the total element concentration in the sediment plus sand mixture. Arsenic recoveries from closed-system (i.e., no gas purging) acid extractions are highly dependent on AVS concentration. Less than 20% of the total arsenic concentration is recovered at AVS concentrations of >0.1 wt % (Figure 8A). At the minimum AVS concentration prepared (0.03 wt %), ~80% of the arsenic in the total sediment mixture was recovered in the closed-system experiments. Arsenic recoveries also depend on AVS concentrations in open systems (with nitrogen gas purging), but greater recovery is obtained compared to closed systems at equivalent AVS concentrations. This is due to H_2S loss from the system at a greater rate with continuous gas purging, which would tend to reduce oversaturation with respect to arsenic sulfide (Figure 8A). In a parallel set of experiments, molar [As]/[AVS] was varied from 0.03 to 1.0 by adding aliquots of 200 mg L^{-1} $NaAsO_2$ to maintain a constant total arsenic concentration of ~1100 μg g^{-1} (Figure 8B). The efficiency of arsenic extraction increases with increasing [As]/[AVS] or as the pool of extractable arsenic available for reaction overwhelms that of hydrogen sulfide. These results indicate that the effect of arsenic sulfide precipitation in sulfidic sediments during acid extraction will increase with decreasing [As]/[AVS] and with decreasing extractant volume-to-sediment mass ratios used in extraction procedures.

The percentage of Pb and Zn (data not shown) extracted is independent of AVS concentration and whether the extraction is carried out in an open or closed system (Figure 8C). These observations demonstrate that Pb and Zn recovery is unaffected by AVS concentrations, which is consistent with predictions based upon solubility calculations. The observed behavior of copper during acid extraction parallels that of arsenic, suggesting the importance of copper sulfide precipitation as predicted with the equilibrium modeling previously described (Figure 8D). In general, more arsenic and copper are detected in acid leaches from materials with

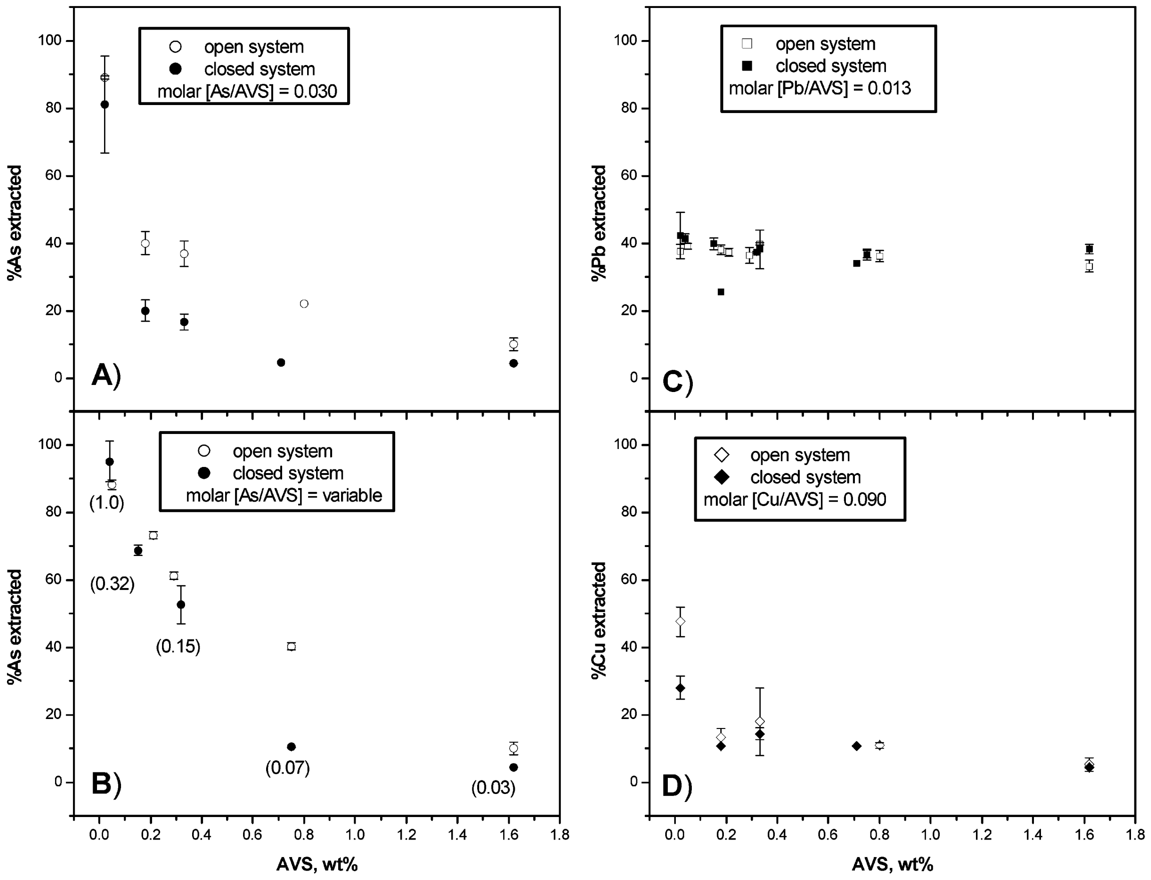

FIGURE 8. Extraction test results using mixtures of HBHA pond sediment with quartz sand in open and closed systems. (A) Percent arsenic extracted at constant molar [As]/[AVS] = 0.030, (B) percent arsenic extracted with variable molar [As]/[AVS] indicated in parentheses, (C) percent lead extracted at constant molar [Pb]/[AVS] = 0.013, and (D) percent copper extracted at constant molar [Cu]/[AVS] = 0.090.

TABLE 1. Arsenic Extraction Efficiency of Arsenic-Bearing Iron Monosulfides and HBHA Pond Sediments and Sediment Mineralogy and Chemical Properties[a]

	3 M HCl	1 M $MgCl_2$	0.1 M Na_2CO_3	0.1 M Na_2S
FeS plus As	0.15 ± 0.10 $n = 5$	1.6 ± 1.5 $n = 8$	20.7 ± 6.0 $n = 8$	85.1 ± 5.3 $n = 5$
HBHA pond sediment	3.8 ± 2.8 $n = 3$	14.6 ± 3.0 $n = 4$	80.1 ± 6.2 $n = 4$	79.8 ± 6.1 $n = 2$

Concentrations of C, S, Fe, As, Pb, and Zn	
total organic carbon	18.3 (±1.5) wt %
total inorganic carbon	0.27 (±0.02) wt %
total sulfur	3.75 (±0.21) wt %
acid-volatile sulfide	1.68 (±0.08) wt %
chromium-reducible sulfur	1.97 (±0.08) wt %
Fe	16.8 (±0.2) wt %
As	1180 (±50) $\mu g\ g^{-1}$
Pb	1360 (±20) $\mu g\ g^{-1}$
Zn	6480 (±250) $\mu g\ g^{-1}$

[a] All values expressed as percent of total arsenic. Extraction time was 1 h. Mean ± 1 SD and number of extraction tests (n) are tabulated. HBHA pond sediment (SC1299-1) was collected from a water depth of 2.2 m. Bulk mineralogy consists of quartz, potassium feldspar, and muscovite.

AVS <0.1 wt % than might be expected based upon the modeling efforts. This could be due to an inaccurate or incomplete thermodynamic database or the fact that rates of metal and sulfide release, rates of metal sulfide precipitation, and the rate of H_2S volatilization are not accounted for in the equilibrium modeling.

Chemical extractions with hydrochloric acid for arsenic in sulfidic sediments and soils may not target the AVS fraction, and therefore, the extent to which arsenic is associated with AVS forms in sulfidic sediments remains equivocal. Not surprisingly, previous studies have reported comparatively small fractions of arsenic partitioned to AVS phases when HCl was used as an extractant (*23*, *25*, *26*). Results of this study indicate that iron monosulfides are potential sinks for arsenic in anoxic sediments (Figure 3). In addition to hydrochloric acid, we tested other extractant solutions including magnesium chloride, sodium carbonate, and sodium sulfide. Magnesium chloride was selected to determine whether arsenic sorbed to mackinawite was loosely bound, and sodium carbonate and sodium sulfide to evaluate extraction efficiency at high pH (see Figure 1) and in the presence of potential ligand-forming species (*41*, *42*). Values in Table 1 are the percentage of arsenic recovered by each of the tested leach solutions. Recovery of arsenic from mackinawite was poor with HCl and $MgCl_2$ and partial with sodium carbonate. However, 85% recovery was achieved with Na_2S, which corresponds to the arsenic recovery obtained at the highest degree of sediment dilution or lowest AVS concentration (Figure 8). A significant fraction of arsenic contained in HBHA pond sediment is extractable with $NaCO_3$ or Na_2S, which suggests that arsenic is associated with iron monosulfides, hydrous ferric oxides, organic materials, or other base-extractable sediment components.

Implications for Sediment Characterization. As pointed out by Cooper and Morse (*20*), metal sulfide extractions using hydrochloric acid are not straightforward. Tests with model iron sulfides and AVS-bearing sediments confirm predictions made with MinteqA2 on the behavior of arsenic in low-pH sulfidic solutions. Results indicate that arsenic sulfides, poorly crystalline orpiment, or alacranite, precipitate as As and H_2S are released from sediment components during acid extractions. Two potential artifacts complicate the use of low-pH extractions for As solid-phase partitioning in sediments containing AVS. If orpiment is present in sediment, it will not be efficiently dissolved with hydrochloric acid. Arsenic sulfides (orpiment, realgar, alacranite) have broad stability fields at low pH; the solubility of these minerals increases with increasing pH and concentration of dissolved sulfide. A more serious problem, however, relates to interpretations of arsenic extraction data. During acid extraction, arsenic may be released from labile sediment components, i.e., loosely bound or sorbed sites. If AVS is present, arsenic sulfide is expected to precipitate at low pH and thereby significantly impact arsenic partitioning by transferring arsenic from a labile and potentially bioavailable fraction to what would be considered, using conventional interpretations, a refractory, biounavailable fraction (i.e., a fraction insoluble in hydrochloric acid). Based upon the results of equilibrium modeling and batch experiments, this artifact occurs over a wide range of AVS concentrations and molar [AS]/[AVS] ratios typically encountered in natural and impacted systems. It should be noted that sequential extraction procedures could be carefully designed to minimize the effect described here by removing arsenic sorbed to FeS or other phases prior to acid extractions using hydrochloric acid (*24*). Chemical extraction procedures still provide the simplest, most practicable tool for evaluating reactive phases and metal associations in sediments and soils. However, there is a continuing need to evaluate the performance of these methods.

Acknowledgments

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Supporting Information Available

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information
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On the use of hydrochloric acid for determining solid-phase partitioning in sulfidic sediments
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A.1. Modifications to MinteqA2 thermochemical database.

Equilibrium expressions in MinteqA2 are composed using a finite number of components, which are the basis entities from which all species in the database can be composed. We have made several changes or additions to the MinteqA2 database with regard to sulfide mineral solubility and aqueous thioarsenic species (Table A.1). An example that demonstrates the procedure for modifying reported thermochemical data to conform to the MinteqA2 format is shown below.

Mineral Solubility. Mineral solubility equilibrium expressions are written as formation reactions within the MinteqA2 thermochemical database. For example, Eary *(1)* reports the solubility for a disordered form of orpiment as $\log K_{sp} = -11.9$ at 25 °C. The reaction was written as,

$^1/_2\ As_2S_{3(am)} + 3H_2O \leftrightarrow H_3AsO_3^0 + {^3/_2}\ H_2S^0$.

Within MinteqA2, this expression must be written using the components H_2O, H^+, HS^{-1}, and $H_3AsO_3^0$. In addition, the expression must be reconfigured to be consistent with a formation reaction. As a first step, the reported solubility expression was multiplied by a factor of 2 to normalize the reaction such that the solid had unit stoichiometry.

$As_2S_{3(am)} + 6H_2O \leftrightarrow 2H_3AsO_3^0 + 3H_2S^0$ $\qquad \log K_{sp} = -23.8$ $\qquad$ Eq. A.1.1

Next, the reaction was modified to replace H_2S^0 with the products of its first deprotonation reaction, H^+ and HS^-. The following expression was added to Eq. A.1.1, as derived from Eary *(1)*,

$3H_2S^0 \leftrightarrow 3HS^- + 3H^+$ $\qquad \log K = -20.982$ $\qquad$ Eq. A.1.2

The resultant expression, following inversion to be consistent with a formation reaction was

$2H_3AsO_3^0 + 3HS^- + 3H^+ \leftrightarrow 6H_2O + As_2S_{3(am)}$ $\qquad \log K_f = 44.8$ $\qquad$ Eq. A.1.3

The number of significant figures for this value is consistent with the value reported by Eary *(1)*. Unit activity was assumed for the solid at standard temperature and pressure and zero ionic strength. This revised value is shown in Table A.1.1 adjacent to the compound labeled 'Orpiment, disordered'.

Table A.1.1. Compilation of changes or additions to MinteqA2 thermochemical database. Mineral solubility and thioarsenite specie equilbria are written as formation reactions; components with positive stoichiometry are defined as reactants while components with negative stoichiometry are products.

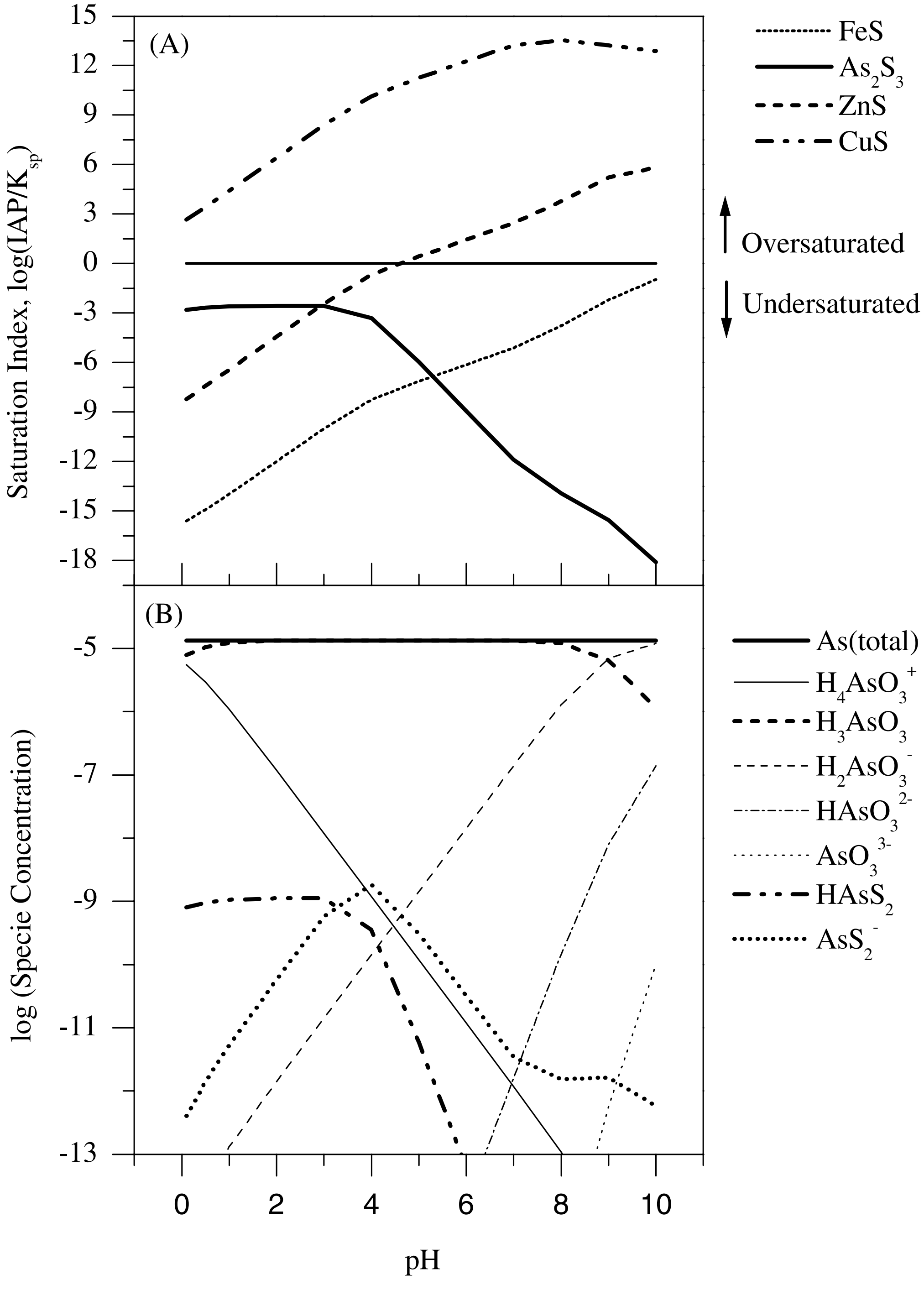
Compound		log K (1)		Component Stoichiometry for Equilibrium Mass Action Equation							
		MinteqA2 (2)	Revised	H_2O	H^+	HS^{-1}	H_3AsO_3	Fe^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}
Orpiment, disordered		--	44.8 (3)	-6.00	3.00	3.00	2.00	--	--	--	--
Orpiment (As_2S_3)		60.9710	46.2 (4)	-6.00	3.00	3.00	2.00	--	--	--	--
FeS, disordered		3.9150	2.96 (5)	--	-1.00	1.00	--	1.00	--	--	--
Mackinawite (FeS)		4.6480	3.68 (6)	--	-1.00	1.00	--	1.00	--	--	--
ZnS, disordered		9.0520	10.89 (7)	--	-1.00	1.00	--	--	1.00	--	--
Sphalerite (ZnS)		11.6180	11.48 (8)	--	-1.00	1.00	--	--	1.00	--	--
CdS, disordered		--	12.28 (7)	--	-1.00	1.00	--	--	--	1.00	--
Greenockite (CdS)		15.9300	14.36 (9)	--	-1.00	1.00	--	--	--	1.00	--
Covellite (CuS)		--	20.95 (10)	--	-1.00	1.00	--	--	--	--	1.00
Thioarsenite	$HAsS_2$	--	21.3 (11)	-3.00	2.00	2.00	1.00	--	--	--	--
	AsS_2^-	--	17.6 (11)	-3.00	1.00	2.00	1.00	--	--	--	--

1) log K values are expressed for standard temperature and pressure at zero ionic strength
2) log K values reported are those included in the 1991 MinteqA2 database
3) Eary, 1992
4) Webster, 1990
5) Davison, 1991
6) Benning et al., 2000
7) Gammons and Frandsen, 2001
8) Daskalakis and Helz, 1993
9) Daskalakis and Helz, 1992
10) Shea and Helz, 1988
11) Developed using data reported by Clarke and Helz (2000) and Ferguson and Gavis (1972).

A.2. Mineral saturation state and arsenic speciation at the AVS detection limit.

The detection limit for AVS determination has been reported as 0.0009 wt% (*11*). Model results were determined for a system with 0.0009 wt% FeS and 100 ppm of As, Cu, and Zn to determine if orpiment solubility was still exceeded during AVS extraction. The results of this modeling effort are shown in Figure A.2.1. At this level of AVS-extractable FeS, the system remains undersaturated with respect to the solubility of a disordered orpiment. These results suggest that sediments with a low content of soluble sulfide may not be subject to the arsenic re-precipitation artifact. However, one must evaluate whether the mass of extracted arsenic can realistically be attributed to a sulfidic phase, or whether it may be associated with a non-sulfidic phase that is dissolved during AVS extraction.

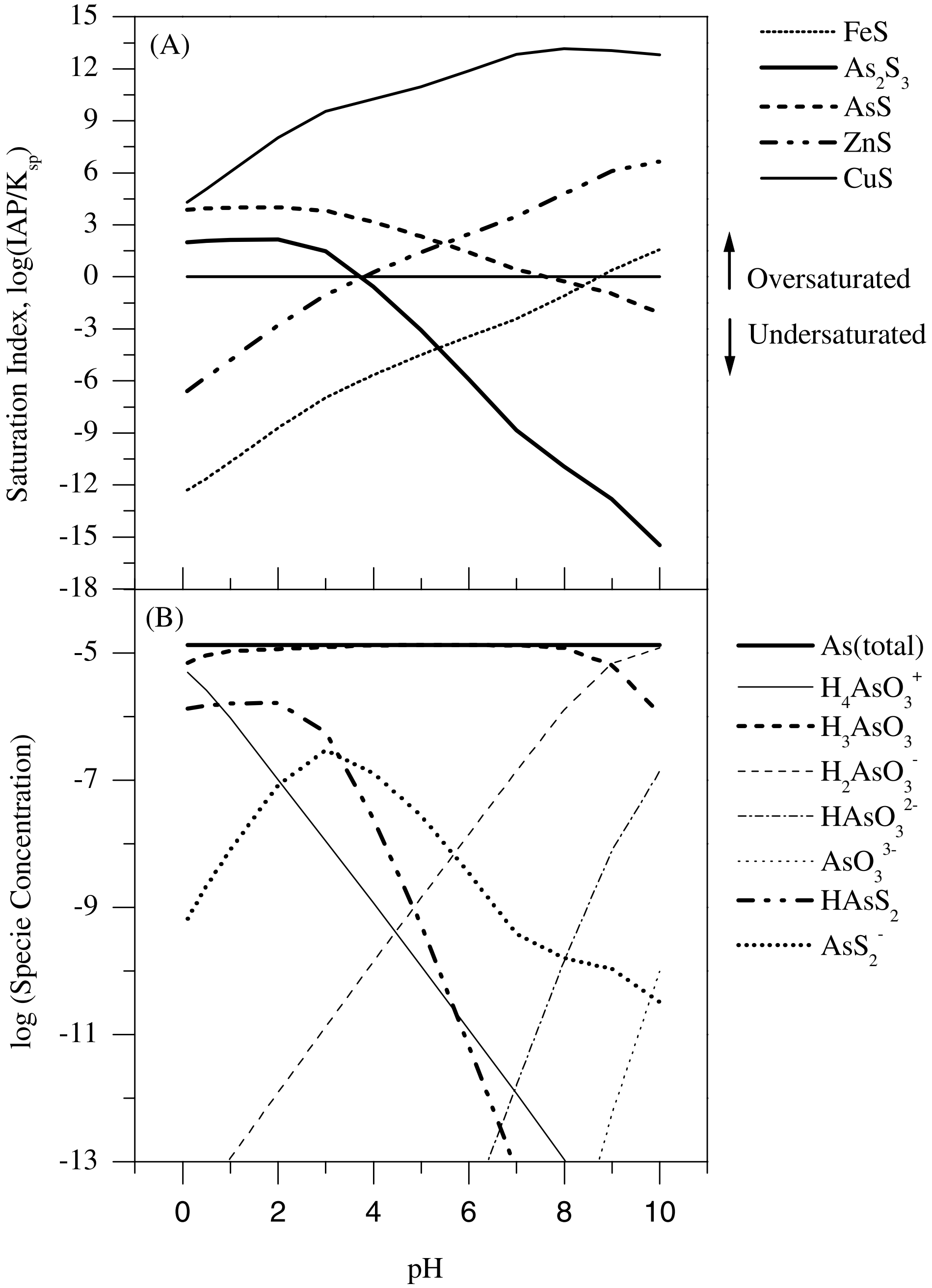
Figure A.2.1. Results of thermodynamic modeling for a system containing 0.4 g sediment with 0.0009 wt% FeS and 100 ppm of As, Cu, and Zn. The FeS and associated metals were allowed to dissolve in a closed system containing 40 mL of 2M NaCl over a range of pH. A) Predicted saturation index as a function of pH for the mineral covellite (CuS) and the disordered forms of FeS, As_2S_3, and ZnS. B) Predicted aqueous arsenic speciation as a function of pH.



A.3. Mineral saturation state and arsenic speciation for a system bounded by the H_2O-H_2 reduction-oxidation equilibrium.

Tuttle et al. (*12*) have suggested the use of $SnCl_{2(s)}$ as a redox buffer during AVS extraction. In order to evaluate the influence of Eh on sulfide mineral solubility during extraction, we performed equilibrium modeling assuming that the system redox was controlled by the H_2O-H_2 equilibrium. This lower redox bound was used, since the predicted Eh for the SnO_2-Sn^{2+} couple was below the stability field of water. An Eh was calculated at each pH using the relationship, Eh(v) = -0.06pH. The results of this modeling effort are shown in Figure A.3.1 for a system with 0.1 wt% FeS and 100 ppm As, Cu, and Zn. Under these conditions, the system is oversaturated with respect to disordered orpiment (As_2S_3) up to pH 3.7. The system is also oversaturated with respect to crystalline realgar (AsS; solubility for a disordered phase unavailable) up to pH 7.6. The measured Eh for a pH = 0.5 solution of HCl-$SnCl_2$ was 45 mV using a platinum electrode. However, this higher Eh value (relative to the H_2O-H_2 equilibrium) did not significantly alter solution saturation with respect to realgar. Thus, this modification to the AVS extraction is also subject to artifacts with respect to arsenic solid phase speciation. Note that the MinteqA2 database (or any other database) does not include thermodynamic data for alacranite, the phase we observe to precipitate at low pH and in the presence of $SnCl_2$. Data for realgar are available and realgar is similar in composition and structure to alacranite. Therefore the saturation state of realgar serves as a useful comparison for that of alacranite.

Figure A.3.1. Results of thermodynamic modeling for a system containing 0.4 g sediment with 0.1 wt% FeS and 100 ppm of As, Cu, and Zn. The FeS and associated metals were allowed to dissolve in a closed system containing 40 mL of 2M NaCl over a range of pH. The Eh of the system was assumed to be in equilibrium with the H_2O-H_2 couple. A) Predicted saturation index as a function of pH for the mineral covellite (CuS), realgar (AsS), and the disordered forms of FeS, As_2S_3, and ZnS. B) Predicted aqueous arsenic speciation as a function of pH.



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